Supporting Information

Nonproductive Events in Ring-Closing Metathesis using Ruthenium Catalysts

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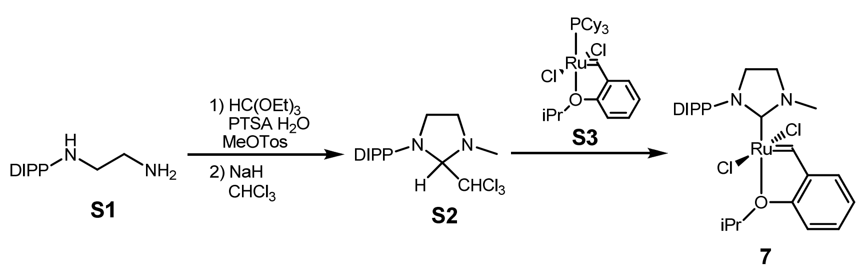
General Information.

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere unless otherwise specified. All solvents were purified by passage through solvent purification columns and further degassed with argon.[1] NMR solvents were dried over CaH_2 and vacuum transferred to a dry Schlenk flask and subsequently degassed with argon. Commercially available reagents were used as received unless otherwise noted. Silica gel used for the purification of organometallic compounds was obtained from TSI Scientific, Cambridge, MA (60 Å, pH 6.5-7.0).

Catalysts **1**, **2**, **3**, and **4** are commercially available and were used as received. **5**[2] and **6**[3] were prepared according to the literature procedure.

Productive TONs were measured using an Agilent 6850 Network GC equipped with a HP-1 column (L = 30 m, I.D. = 0.32 mm, Film = 0.25 µm). Response factors were calculated for all compounds prior to determining conversion. Degenerate TONs were measured with an Agilent 6200 Series TOF LC/MS equipped with an Agilent 1200 series HLPC stack using a 100% MeCN Direct Inject method.

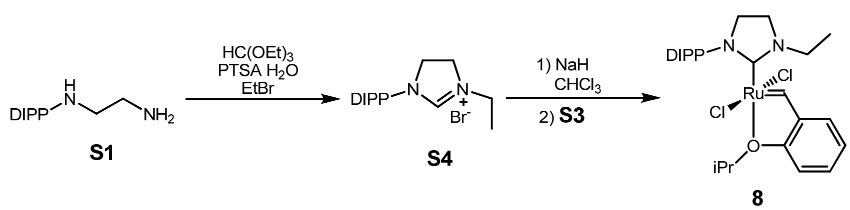
Synthesis of 7.



S1[4] (91 mg, 0.41 mmol), methyl tosylate (92 mg, 0.49 mmol), PTSA·H_2O (4 mg, 0.02 mmol), $CH(OEt)_3$ (0.9 mL), and toluene (0.9 mL) were placed in a 20 mL scintillation vial and sealed under air using a teflon cap. The sealed vial was heated to 110 °C for 14 h and then allowed to cool to RT. Et_2O was added to precipitate the product and the solution was stirred for 2 h after which the solvent was decanted off and the remaining solid dried under vacuum. The crude product (280 mg, 0.67 mmol) was dissolved in dry $CHCl_3$ (10 mL) in a Schlenk flash and

95% NaH (97 mg, 4.0 mmol) was added in portions. The flask was sealed and heated to 55 °C for 14 h. After cooling, the solution was diluted with Et_2O and passed through a pad of silica gel. The filtrate was concentrated without heating and used without further purification. A 50 mL round-bottom flask was dried and charged with **S2** (112 mg, 0.34 mmol), **S3** (103 mg, 0.17 mmol), and THF (20 mL). The flask was heated to 70 °C under argon for 10 h and then concentrated. The residue was dissolved in a minimal amount of C_6H_6 and purified by flash chromatography on silica gel eluting with 10% Et_2O/Pentane to collect a brown band (**S3**), and then 30% Et_2O/Pentane to collect a green/tan band (**7**, 7 mg, 7%). ^{1}H NMR (500 MHz, C_6D_6): δ 1.04 (m, 6H), 1.11 (m, 6H), 1.72 (m, 6H), 2.92 (m, 2H), 3.34 (m, 4H), 3.82 (s, 3H), 4.63 (sept, *J* = 3.5 Hz, 1H), 6.42 (dd, *J* = 8.5 Hz, *J* = 3.5 Hz, 1H), 6.67 (dt, *J* = 7.5 Hz, 4 Hz, 1H), 7.08 (m, 2H), 7.19 (dd, *J* = 7.5 Hz, *J* = 4 Hz, 2H), 7.36 (dt, *J* = 8 Hz, 4 Hz, 1H), 16.33 (s, 1H). ^{13}C NMR (126 MHz, C_6D_6) δ 270.08, 211.51, 153.58, 149.32, 148.20, 144.18, 138.64, 130.10, 129.19, 128.66, 125.44, 122.81, 122.37, 113.49, 107.56, 75.51, 55.44, 51.29, 38.79, 30.54, 28.49, 26.03, 24.57, 22.52. HRMS (FAB+): Calculated: 564.1249, Found: 562.1240.

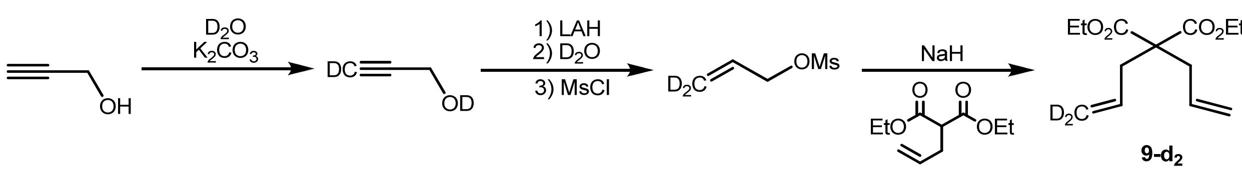
Synthesis of 8.



S1 (202 mg, 0.917 mmol), EtBr (82 µL, 1.1 mmol), PTSA·H_2O (9 mg, 0.05 mmol), $CH(OEt)_3$ (2.25 mL), and toluene (2.25 mL) were placed in a 20 mL scintillation vial and sealed under air using a Teflon cap. The vial was heated to 110 °C for 16 h, after which it was cooled to RT and the toluene was removed *in vacuo*. Et_2O (ca. 8 mL) was added to the resulting solution and it was stirred vigorously for 1 h. The Et_2O was decanted off and the remaining precipitate was washed with copious amounts of Et_2O and dried under vacuum. Flash chromatography on silica gel using 7% MeOH:CH_2Cl_2 gave **S4** (92 mg, 30%) as an off white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.34 – 7.27 (m, 1H), 7.11 (d, *J* = 7.8 Hz, 2H), 4.33 – 4.24 (m, 2H), 4.17 – 4.07 (m, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 2.78 (dt, *J* = 13.6, 6.8 Hz, 2H), 1.32 – 1.24 (m, 4H), 1.15 (dd, *J* = 6.8, 3.8 Hz, 12H).

S4 (64 mg, 0.189 mmol) was placed in a 20 mL vial followed by dry $CHCl_3$ (2 mL). 95% NaH (23 mg, 0.945 mmol) was added in small portions after which the vial was sealed under nitrogen and heated to 55 °C for 10 h. After cooling to RT, the solution was diluted with Et_2O, filtered through a small pad of silica washing with Et_2O, and conc. without heating to give the chloroform adduct (48 mg, 67%) which was used without further purification. A 100 mL RB flask was dried and charged with the chloroform adduct (306 mg, 0.81 mmol), **S3** (361 mg, 0.60 mmol), and THF (50 mL). The RB was heated to 70 °C for 24 h after which it was cooled to RT and conc. *in vacuo*. The resulting residue was dissolved in a minimal amount of PhH and flashed on silica gel using 30% Et_2O/Pentane to collect the left over **S3** followed by 60% Et_2O/Pentane to collect **8** (40 mg, 9%). ^{1}H NMR (500 Mhz, C_6D_6): δ 1.01 (d, 6H, J = 6.6 Hz), 1.09 (d, 6H, J = 6.6 Hz), 1.28 (t, 3H, J = 6.6 Hz), 3.05 (m, 2H), 3.30 (sept, 2H, 6.6 Hz), 3.42 (m, 2H), 4.50 (d, 2H, J = 6.6 Hz), 4.59 (sept, 1H, J = 6 Hz), 6.38 (d, 1H, J = 8.4 Hz), 6.65 (dt, 1H, J = 7.2 Hz, J = 1.2 Hz), 7.04-7.08 (m, 2H), 7.11 (br s, 3H), 7.16 (s, 1H), 7.17 (s, 1H), 7.33 (t, 1H, J = 7.8 Hz), 16.32 (s, 1H). ^{13}C NMR (151 MHz, C_6D_6) δ 285.32, 210.77, 153.55, 150.67, 149.36, 144.29, 138.68, 130.08, 129.21, 128.90, 128.66, 125.44, 122.82, 122.46, 113.51, 75.41, 55.37, 47.67, 47.25, 28.53, 26.04, 24.59, 22.52, 14.19. HRMS (FAB+): Calculated: 578.1405, Found: 578.1433.

Synthesis of 9-*d*$_2$

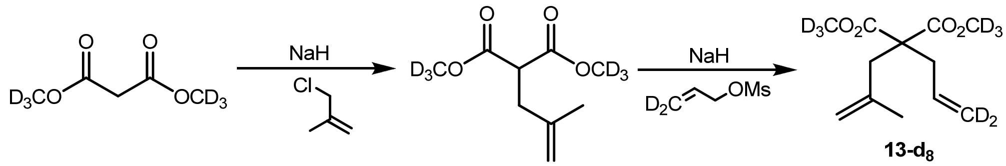


Propargyl alcohol (4 mL, 67.7 mmol), K_2CO_3 (2.8 g, 20.3 mmol), and D_2O (12 mL, Aldrich 99.9%) were combined in a Biotage 20 mL microwave vial with a stir bar. Two other vials with the same reagents were prepared and all three were microwaved at 100 °C for 10 min using a Biotage Initiator microwave. The three vials were combined in a separatory funnel and NaCl was added. The aqueous layer was extracted with Et_2O (3X) and the organic layers were combined, dried with Na_2SO_4, and carefully conc. to yield deuterated propargyl alcohol showing ca. 90% D incorporation. The same procedure was repeated to obtain deuterated propargyl alcohol (7.06 g, 60%) with >96% incorporation after distillation under Ar. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.23 (s, 2H).

A 250 mL round-bottomed flask was dried and charged with $LiAlH_4$ (4.94 g, 130 mmol), and Et_2O (150 mL) in a glovebox. The flask was capped with an addition funnel, removed from the box and cooled to 0 °C under Ar. Propargyl alcohol-d_2 (7.06 mL, 121.6 mmol) was dissolved in Et_2O (28 mL) and added to the addition funnel. The alcohol solution was added dropwise to the LAH suspension at 0 °C over a period of 1 h after which the solution was allowed to warm to RT and stirred for 6 h. D_2O (5 mL) was added slowly at 0 °C followed by a 15 wt% NaOH in D_2O solution (5 mL). Finally, D_2O (15 mL) was added quickly and the suspension was allowed to stir at RT overnight. $MgSO_4$ and celite were added and the suspension was filtered through celite, washing with Et_2O, and the filtrate was conc. Allyl alcohol-d_3 (4 g, 55%) was recovered via fractional distillation under Ar (INSERT BOILING POINT). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.98 (m, 1H), 4.14 (t, J = 6 Hz, 2H). A 250 mL RB flask was dried and charged with dry triethylamine (6.4 mL, 44.9 mmol), allyl alcohol-d_3 (2.5 g, 40.8 mmol), and Et_2O (120 mL) and cooled to 0 °C. MsCl (3.5 mL, 44.9 mmol) was added dropwise and the reaction was stirred at 0 °C for 1 h after which it was warmed to RT and stirred for 12 h. The reaction was quenched with H_2O, and the aqueous layer was extracted with Et_2O (3X). The organic layers were combined and stirred with sat. $NaHCO_3$ for 30 minutes after which the org. layer was separated, washed with brine, and dried with $MgSO_4$, and conc. to yield mesylate-d_2 (1.5 g, 26%) which was used immediately without further purification.

A 100 mL round-bottomed flask was dried and charged with 60% NaH (0.48 g, 20.1 mmol) and THF (20 mL). Diethyl allyl malonate (3.2 mL, 15.9 mmol) was added dropwise and the solution was heated to 60 °C for 30 min. After cooling to RT, mesylate-d_2 (0.96 g, 6.9 mmol) was added slowly as solution in THF and the reaction was heated to 60 °C for 12 h. After cooling to RT, the reaction was quenched with sat. NH_4Cl and the aq. layer was extracted with Et_2O (2X). The organic layers were combined, dried over Na_2SO_4 and conc. to give the crude product which was purified via flash chromatography on silica gel (5% EtOAc/Hexanes) to give **9-d_2** (1.87 g, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.65 (dddd, J = 14.8, 10.7, 9.3, 7.4 Hz, 1H), 5.14 – 5.07 (m, 1H), 4.22 – 4.13 (m, 2H), 2.63 (dd, J = 7.4, 1.3 Hz, 2H), 1.27 – 1.22 (m, 3H). ^{13}C NMR (151 MHz, $cdcl_3$) δ 170.65, 132.27, 132.04, 119.02, 61.12, 57.17, 36.67, 36.57, 14.04. HRMS (FAB+): Calculated: 243.1570, Found: 243.1560.

Synthesis of 13-d_8



A 100 mL round-bottomed flask was dried and charged with 60% NaH (0.92 g, 38 mmol) and THF (30 mL). Dimethyl malonate-d_6[5] (2.5 mL, 20.9 mmol) was added dropwise and the reaction was heated to 60 °C for 30 min. After cooling to RT, 1-chloro-2-methyl propene (2.27 mL, 23 mmol) was added dropwise and the reaction was again heated to 60 °C for 12 h. After cooling to RT, the reaction was quenched with sat. NH_4Cl and extracted with Et_2O (3X). The organic layers were combined, dried over Na_2SO_4 and conc. to give the crude product which was purified via flash chromatography (7% EtOAc/Hexanes) on silica gel (2.23 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.78 (s, 3H), 4.71 (s, 4H), 3.61 (td, J = 7.8, 1.9 Hz, 2H), 2.61 (d, J = 7.1 Hz, 7H), 1.73 (s, 10H).

The same alkylation procedure as above with the previous product (1.9 g, 9.8 mmol), mesylate-d_2 (1.5 g, 10.8 mmol), and 60% NaH (0.43 g, 17.9 mmol) yielded **13 - d$_8$** (1.62 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (s, 1H), 4.86 (s, 1H), 4.72 (s, 1H), 2.70 (s, 1H), 2.66 (d, J = 7.4 Hz, 1H), 1.52 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.43, 140.33, 132.35, 117.47, 115.67, 57.23, 40.23, 36.80, 23.02. HRMS (FAB+): Calculated: 235.1780, Found: 235.1796.

Typical Reaction Procedure.

The RCM of **9-d_2** and **13-d_8/13-d_0** using the catalysts described were conducted using a Symyx™ Technologies Core Module (Santa Clara, CA) housed in a Braun nitrogen-filled glovebox and equipped with Julabo LH45 and LH85 temperature-control units for separate positions of the robot tabletop.

For experiments where aliquots were taken during the course of the reaction, the entire operation could be performed on 12 reactions simultaneously in 1 or 2 mL vials by an Epoch software-based protocol as follows. To prepare catalyst stock solutions (1 mM), 20 mL glass scintillation vials were charged with catalyst (5 µmole) and diluted to 5 mL total volume in toluene. Catalyst solutions, 6 to 800 µL depending on desired final catalyst loading, were transferred to reaction vials and solvent was removed via centrifugal evaporation. The catalysts were preheated to 50 °C using the LH45 unit, and stirring was started. Substrates (0.1 mmol), containing dodecane (0.025 mmol) as an internal standard, were dispensed simultaneously to 4 reactions at a time using one arm of the robot equipped with a 4-needle assembly. Immediately following substrate addition, toluene was added to reach the desired reaction molarity. The reaction vials were left open to the glovebox atmosphere during the course of the reaction.

After the 2 minutes required for completion of the transfer, 50 μL aliquots of each reaction were withdrawn using the other robot arm and dispensed to 1.2 mL septa-covered vials containing 5% v/v ethyl vinyl ether in toluene cooled to -20 ^{o}C in two 96-well plates. The needle was flushed and washed between dispenses to prevent transfer of the quenching solution into the reaction vials. 16 time points were sampled at preprogrammed intervals and the exact times were recorded by the Epoch protocol. All reactions were conducted in either duplicate or triplicate in order to ensure reproducibility.

Alternatively, reactions could also be performed on the bench as follows. In a glove box, 126 μL of a stock solution prepared from **9-*d*$_2$** (244 μL, 1 mmol), dodecane (23 μL, 0.1 mmol), and toluene (1 mL) was added to 2 (duplicate) or 3 (triplicate) 4 mL scintillation vials equipped with stir bars. Toluene (0.9 mL) was added and the vials were sealed with septa caps, removed from the box, and heated to 50 °C under a continuous flow of Ar. The desired amount of catalyst (depending on the loading) was injected as a solution in toluene after which 50 μL aliquots were removed over time and injected into chilled GC vials containing toluene and ca. 5% v/v ethyl vinyl ether. Reactions conducted on the bench showed identical behavior to those conducted using the Symyx^{TM} robot. The best results were obtained from the following catalyst loadings:
1 – 1000 ppm, **2, 3, 4, 5** – 250 ppm, **6** – 500 ppm, **7** – 5000 ppm, **8** – 1000 ppm.

Productive TON Determination

Samples for GC analysis were obtained by adding a 50 μL reaction aliquot to 1 mL of toluene containing ca. 5% v/v ethyl vinyl ether at either -10 °C (bench) or -30 °C (robot).

GC response factors were determined for all starting materials and products. Dodecane was used as an internal standard. To determine conversion factors, stock solutions of each compound were prepared and used to make various solutions at different [substrate]/[dodecane] ratios. The ratio of the area percent data was plotted against the molar ratio of each solution and the corresponding factor was determined by fitting the data to a linear trendline.

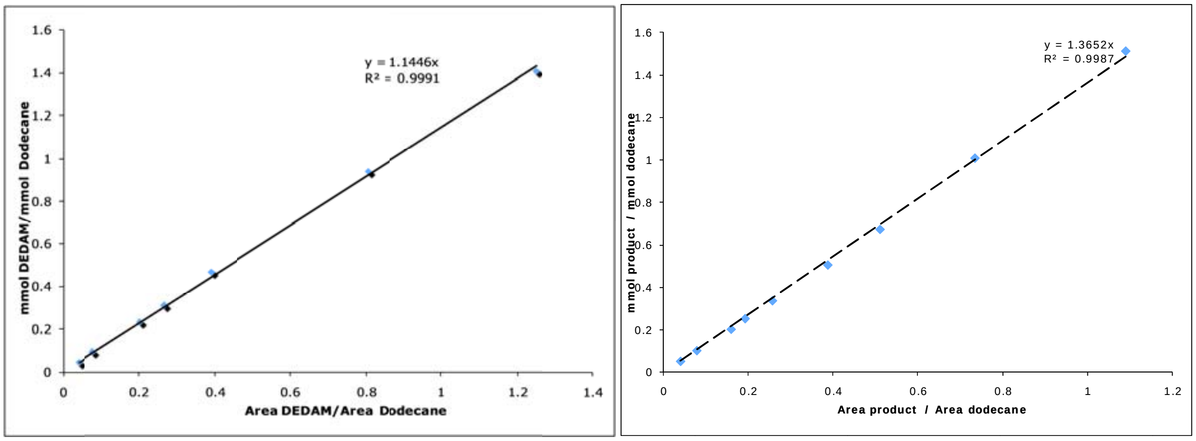


Figure S1. Response factor graphs for **9-*d*$_2$** (left) and **12** (right).

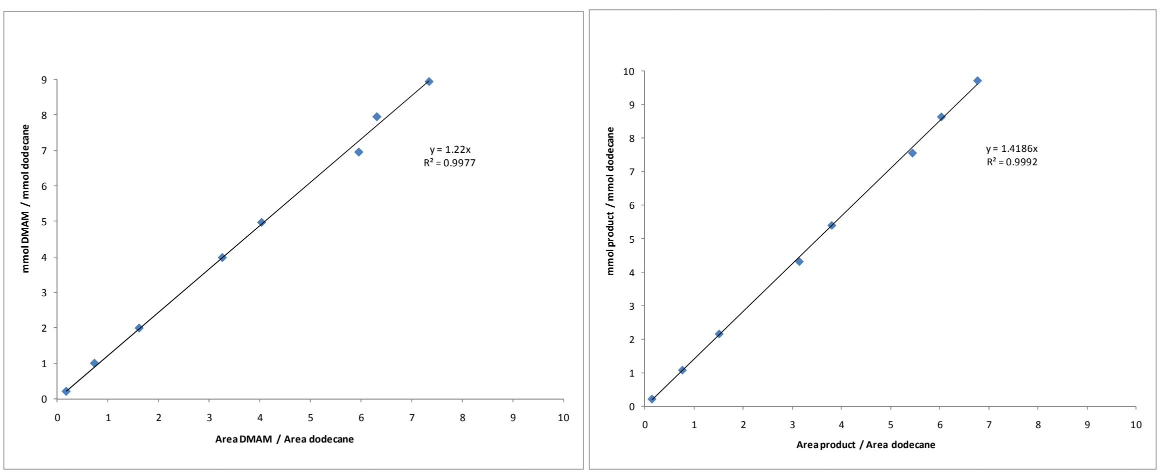


Figure S2. Response factor plots for **13-*d*$_0$+13-*d*$_8$** (left) and **14** (right).

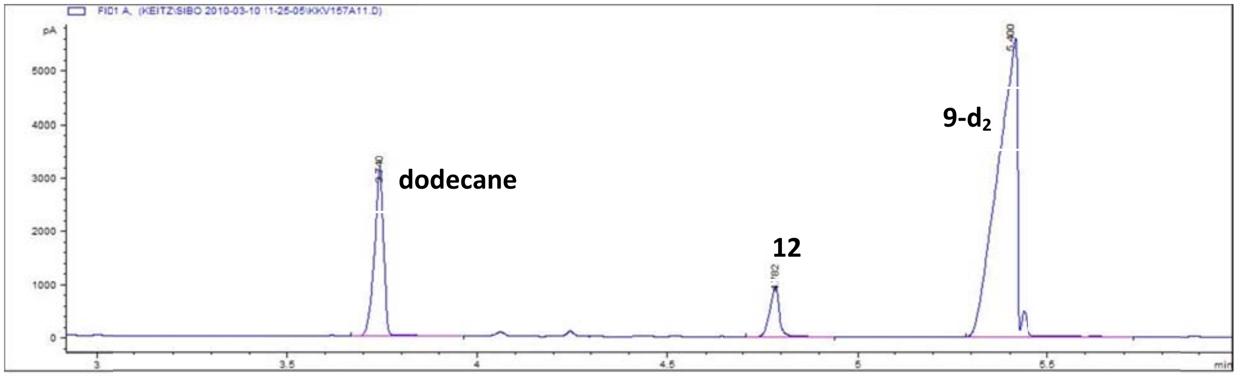


Figure S3. Sample GC chromatogram for **9-*d₂*.**

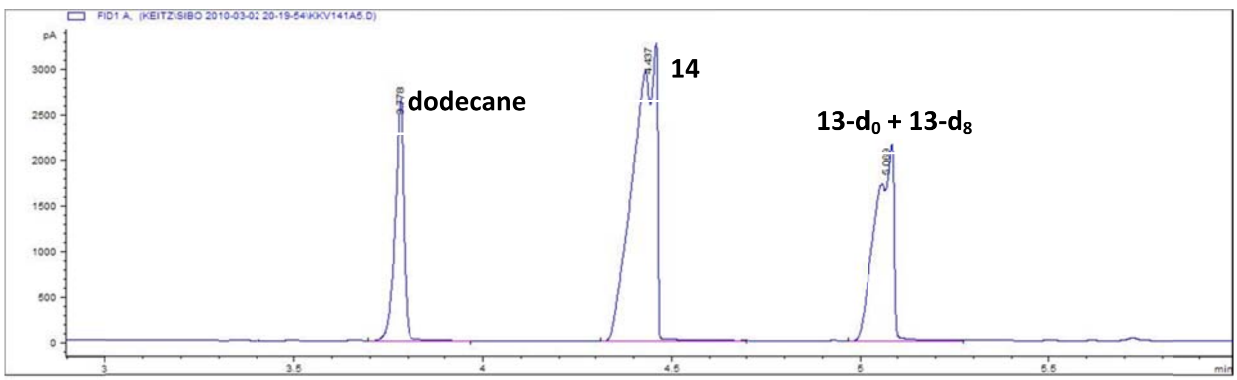


Figure S4. Sample GC chromatogram for **13-d_8** + **13-d_0**.

Instrument conditions: Inlet temperature: 85 °C; Detector temperature: 250 °C; hydrogen flow: 30 mL/min’ air flow: 400 mL/min; constant col + makeup flow: 25 mL/min.

GC Method: 85 °C for 1.5 min, followed by temperature increase of 15 °C/min to 160 °C, followed by a second temperature increase of 80 °C/min to 210 °C with a subsequent isothermal period at 210 °C for 5 min. Total run time was 13.1 min including a 210 °C post-run for 1 min. GC data for each timepoint were analyzed according to the following model spreadsheet.

Table S1. Example for calculation of **9-d_2** conversions.

Aliquot	dodecane	P	SM	ratio P	ratio SM	P (mmol)	SM (mmol)	conv.
1	**A**	**B**	**C**	**B/A**	**C/A**	0.01[1.37(**B/A**)]	0.01[1.14(**C/A**)]	P (mmol)/[P (mmol) + SM (mmol)]

Nonproductive TON determination.

Aliquots taken as above were injected (0.75 µL) into an Agilent 6200 Series TOF LC/MS instrument using a direct-inject 100% MeCN method. Relative isotopologue counts were obtained from the positive ion spectra and showed good reproducibility when the same sample was injected multiple times.

A typical spreadsheet used to calculate the number of degenerate TONs is shown below (Table S2). Using the LCMS-TOF, the counts of **9-d_0** and **9-d_4** were determined and used to compute a conversion after subtracting the corresponding values for the stock solution (to account for any isotopologues already present, not shown in Table S2). Conversions that resulted in negative values were thrown out. The conversions to **9-d_0** and **9-d_4** were then each multiplied by 2 and summed together to obtain the total degenerate conversion. This factor of 2 helps account for the degenerate processes that generate the same isotopologue (e.g., **9-d_0** reacting with $RuCH_2$ to form **9-d_0**). Finally, the degenerate TONs are calculated based on the catalyst loading and compared to the productive TONs which were calculated as above. The raw data also follows.

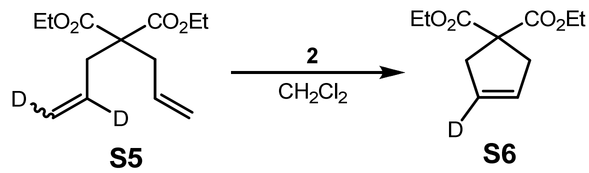
Table S2. Example for calculation of **9-d_2** degenerate TONs.

Loading (ppm)	Well	9-d0	9-d2	9-d4	9-d4/9-d0	9-d0/9-d2	9-d4/9-d2	conv to 241	conv to 245	degen	Degen TON	% conv	Prod TON
L	A1	A	B	C	C/A	A/B	C/B	A/(A+B+C)	C/(A+B+C)	2*A/(A+B+C) + 2*C/(A+B+C)	[2*A/(A+B+C) + 2*C/(A+B+C)]/(L/1e6)	X	X/(L/1e6)

Reversibility of the RCM reaction.

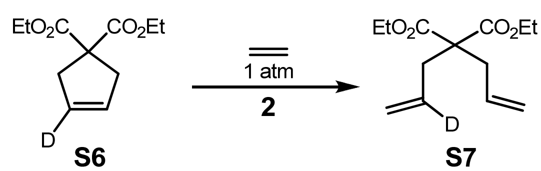
Recent work by Piers and coworkers has shown that a sufficiently active metathesis catalyst may react with cyclic olefins (such as those typically generated as products of RCM) to form an alkylidene product.[6] In order to test for this possibility, the following experiments were performed.

Synthesis of S6.



S5[7] (200 μL, 0.825 mmol) was placed in a dry 10 mL RB flask and dissolved in CH_2Cl_2 (5 mL). Catalyst **2** (17 mg, 0.021 mmol) was added in one portion and the reaction was stirred at RT under Ar for 1 h. The solvent was removed *in vacuo* and the remaining brown residue was purified via Kugelrohr distillation (ca. 60 mTorr, 110 °C) to yield **S6** (160 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$ δ 5.60 (s, 1H), 4.31 – 4.08 (m, 4H), 3.00 (s, 4H), 1.37 – 1.15 (m, 6H). HRMS (FAB+): Calculated: 214.1184, Found: 214.1186.

Ring-Opening Experiment.



In a nitrogen filled glovebox, an NMR tube was charged with **2** (3 mg, 0.004 mmol) and d8-toluene (distilled from CaH_2, 1 mL). The tube was capped with a rubber septum, removed from the glove box, and **S5** (15 μL, 0.07 mmol) was injected via syringe. The tube was evacuated and backfilled with ethylene (x3) and placed in an oil bath preheated to 50 °C. Monitoring the reaction via ^{1}H NMR spectroscopy revealed no detectable amount of **S6**. Similarly, a 10 mL RB flask was dried and charged with **2** (3 mg, 0.004 mmol), and toluene (1 mL). Compound **S5** (15 μL, 0.07 mmol) was added and the reaction was heated to 50 °C under a continuous flow of ethylene. Aliquots were removed periodically and quenched with ethyl vinyl ether before being subjected to analysis via mass spec. A very small amount of the ring-opened product (**S7**) was detected by high res mass spec (Figure S5).

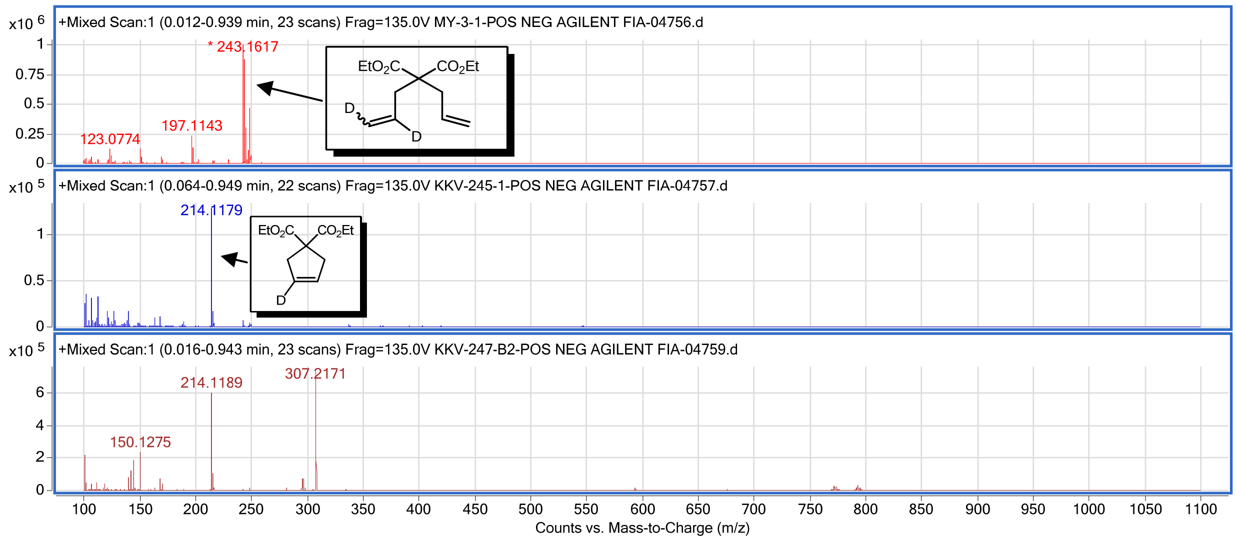


Figure S5. Mass spectrum of **S5** (top), **S6** (middle), and reversibility experiment reaction aliquot (bottom).

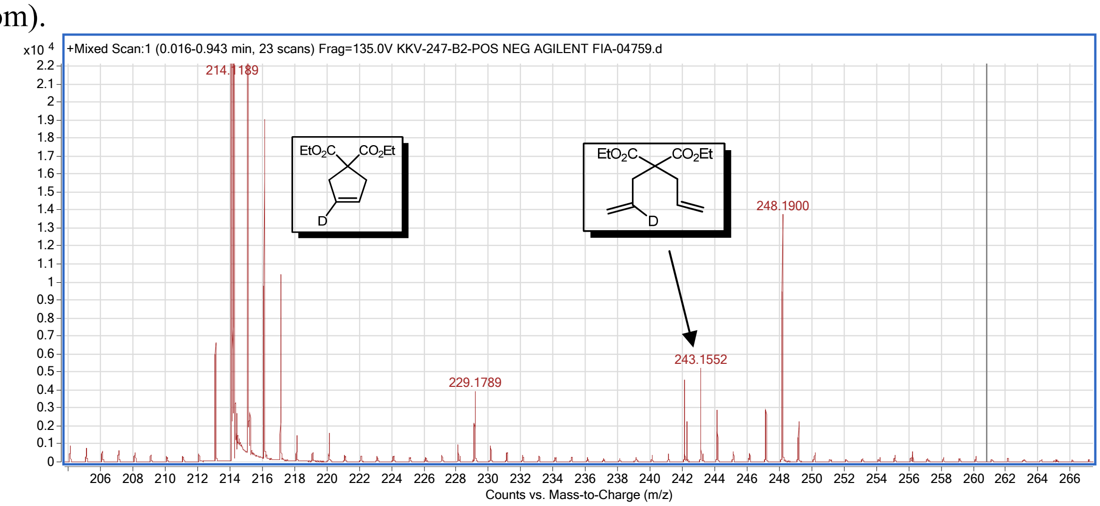
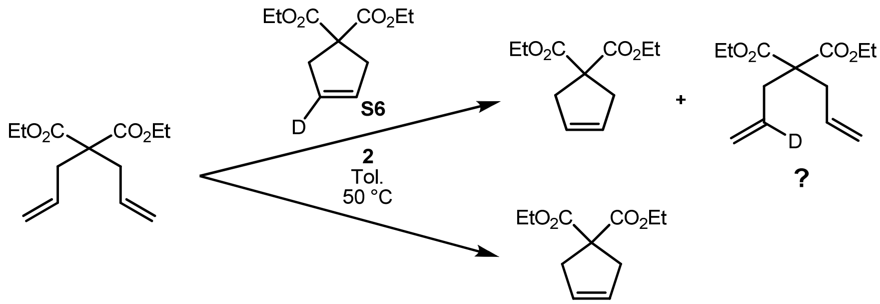


Figure S6. Regional blow up of bottom spectrum in Figure S5 showing presence of ring-opened product **S7**.



Furthermore, when the reaction of catalyst **2** with diethyl diallylmalonate was performed in the presence of **S6**, no significant increase in the amount of **S7** was observed (relative to a control), which indicates that ring-opening followed by olefin termini exchange is not kinetically competitive with other degenerate metathesis pathways.

Based on the results of the above experiments, we conclude that although reversion of the RCM product is possible, it appears to occur relatively infrequently and with such a slow relative rate that it should not significantly impact our results or conclusions.

Catalyst	Cat Loading (ppm)	Timepoir	m/z = 241	m/z = 242	m/z = 243	m/z = 244	m/z = 245	245/241	241/243	245/243	% conv to 24	% conv to 24	% degen	% degen w/o negative	Degen TON	t(h)	% conv	Productive TON	Prod:Degen	Total TON
Stock Solution		0	3250	31617	472593	67691	9441	2.905	0.007	0.020	0.67	1.95	5.23							
C712 (0.05 M)	250	1	1405	12970	215642	27251	4257	3.030	0.007	0.020	-0.03	-0.02	-0.11	0.00	0	0.04	0.00	0	#DIV/0!	0
	250	2	2040	17656	288659	37639	5408	2.651	0.007	0.019	0.02	-0.12	-0.20	0.00	0	0.09	0.00	0	#DIV/0!	0
	250	3	2750	25101	375269	49220	7064	2.569	0.007	0.019	0.04	-0.11	-0.13	0.00	0	0.16	3.17	127	#DIV/0!	127
	250	4	3413	18188	293165	38453	5921	1.735	0.012	0.020	0.46	0.01	0.94	0.94	38	0.24	5.25	210	5.58	248
5	250	5	4043	23250	344492	45556	7636	1.889	0.012	0.022	0.47	0.20	1.33	1.33	53	0.36	8.73	349	6.57	402
	250	6	3426	16247	226214	31207	6002	1.752	0.015	0.027	0.78	0.60	2.77	2.77	111	0.51	15.24	609	5.50	720
	250	7	6402	18107	229188	33003	9739	1.521	0.028	0.042	1.94	2.02	7.93	7.93	317	0.76	34.00	1360	4.29	1677
	250	8	14176	23884	249802	41877	20991	1.481	0.057	0.084	4.30	5.42	19.45	19.45	778	1.26	68.79	2752	3.54	3530
	250	9	2286	2580	22305	4911	2685	1.175	0.102	0.120	7.71	7.90	31.22	31.22	1249	2.01	80.84	3234	2.59	4482
	250	10	2863	3194	26179	5406	3339	1.166	0.109	0.128	8.17	8.37	33.08	33.08	1323	3.01	84.15	3366	2.54	4689
	250	11	2221	2589	19123	4261	2843	1.280	0.116	0.149	8.51	9.81	36.64	36.64	1466	5.01	86.85	3474	2.37	4940
	250	12	2435	3306	23429	4865	3751	1.540	0.104	0.160	7.55	10.72	36.55	36.55	**1462**	8.01	88.88	**3555**	2.43	**5017**
C712 (0.10 M)	250	1	4278	32857	493277	66137	9390	2.195	0.009	0.019	0.17	-0.09	0.16	0.16	6	0.04	2.13	85	13.17	92
	250	2	5104	33500	502775	64089	10040	1.967	0.010	0.020	0.32	-0.01	0.62	0.62	25	0.09	3.82	153	6.18	177
	250	3	4359	26245	387076	49243	8886	2.039	0.011	0.023	0.42	0.27	1.39	1.39	55	0.16	6.60	264	4.76	319
	250	4	6258	31292	442465	60362	10527	1.682	0.014	0.024	0.69	0.35	2.08	2.08	83	0.24	11.03	441	5.30	524
5	250	5	7240	26722	336264	45551	11374	1.571	0.022	0.034	1.37	1.26	5.26	5.26	210	0.36	19.83	793	3.77	1004
	250	6	11977	31897	412421	59763	17803	1.486	0.029	0.043	2.04	2.08	8.24	8.24	330	0.51	34.58	1383	4.20	1713
	250	7	14258	29086	336158	51608	21043	1.476	0.042	0.063	3.17	3.72	13.78	13.78	551	0.76	53.10	2124	3.85	2675
	250	8	18370	29952	313772	52245	26693	1.453	0.059	0.085	4.45	5.49	19.89	19.89	795	1.26	66.52	2661	3.34	3456
	250	9	16178	24832	233914	40817	24238	1.498	0.069	0.104	5.23	6.89	24.23	24.23	969	2.01	73.97	2959	3.05	3928
	250	10	18495	26263	232476	44691	26164	1.415	0.080	0.113	6.00	7.50	27.00	27.00	1080	3.01	78.21	3128	2.90	4208
	250	11	3316	5256	36641	7690	4874	1.470	0.090	0.133	6.73	8.93	31.31	31.31	**1252**	5.01	81.56	**3262**	2.61	**4515**
C823 (1000 ppm)	1000	1	7133	31803	493088	63759	12873	1.805	0.014	0.026	0.72	0.56	2.57	2.57	26	0.04	18.07	181	7.04	206
	1000	2	15802	51905	779123	101717	21585	1.366	0.020	0.028	1.27	0.70	3.93	3.93	39	0.09	26.46	265	6.74	304
	1000	3	8405	25535	360854	50019	13223	1.573	0.023	0.037	1.53	1.51	6.08	6.08	61	0.15	32.66	327	5.37	387
	1000	4	13979	40281	550448	77190	19601	1.402	0.025	0.036	1.72	1.41	6.27	6.27	63	0.24	37.36	374	5.96	436
1	1000	5	17993	46147	623051	87727	24734	1.375	0.029	0.040	2.03	1.77	7.60	7.60	76	0.35	41.38	414	5.44	490
	1000	6	19862	53296	710280	100066	29270	1.474	0.028	0.041	1.95	1.91	7.71	7.71	77	0.50	44.42	444	5.76	521
	1000	7	9517	23429	293456	41592	12196	1.281	0.032	0.042	2.35	1.92	8.55	8.55	85	0.75	47.33	473	5.54	559
	1000	8	21192	50677	640587	94648	28677	1.353	0.033	0.045	2.40	2.21	9.21	9.21	92	1.25	49.91	499	5.42	591
	1000	9	15813	37225	474659	71378	22477	1.421	0.033	0.047	2.41	2.44	9.70	9.70	97	2.00	51.63	516	5.32	613
	1000	10	16380	31892	392821	62300	20434	1.247	0.042	0.052	3.14	2.81	11.91	11.91	119	3.00	52.76	528	4.43	647
	1000	11	19353	44079	530029	79201	27136	1.402	0.037	0.051	2.69	2.76	10.90	10.90	109	5.00	54.14	541	4.97	650
	1000	12	9884	22857	261178	39351	13322	1.348	0.038	0.051	2.81	2.74	11.09	11.09	**111**	8.00	55.31	**553**	4.99	**664**
C571	250	1	0	34260	533421	67929	9928	#DIV/0!	0.000	0.019	-0.67	-0.12	-1.58	0.00	0	0.04	3.23	129	#DIV/0!	129
	250	2	4018	22902	398962	50746	8397	2.090	0.010	0.021	0.31	0.10	0.81	0.81	32	0.09	7.51	300	9.32	333
	250	3	5157	33622	499216	64856	10146	1.967	0.010	0.020	0.33	0.03	0.72	0.72	29	0.16	15.09	604	21.01	632
	250	4	4698	30573	439698	56153	9348	1.990	0.011	0.021	0.37	0.11	0.96	0.96	38	0.24	25.76	1031	26.81	1069
	250	5	3980	24072	370386	47863	8988	2.258	0.011	0.024	0.37	0.40	1.54	1.54	61	0.36	36.46	1458	23.75	1520
4	250	6	1187	6521	88235	12354	2397	2.019	0.013	0.027	0.62	0.67	2.58	2.58	103	0.51	44.29	1772	17.19	1875
	250	7	4896	23611	334100	45441	9703	1.982	0.015	0.029	0.73	0.84	3.14	3.14	126	0.76	51.62	2065	16.42	2191
	250	8	4753	22190	305760	44440	9728	2.047	0.016	0.032	0.81	1.09	3.81	3.81	153	1.26	59.69	2388	15.65	2540
	250	9	4368	19181	225218	35208	8258	1.891	0.019	0.037	1.17	1.53	5.39	5.39	215	2.01	64.51	2580	11.98	2796
	250	10	5898	26039	296740	48143	11637	1.973	0.020	0.039	1.21	1.76	5.93	5.93	237	3.01	67.49	2700	11.38	2937
	250	11	2710	11755	100627	19222	5060	1.867	0.027	0.050	1.83	2.72	9.11	9.11	**364**	5.01	70.05	**2802**	7.69	**3166**
	250	12																	#DIV/0!	0

Figure S7. Data for RCM of **9-d_2**.

C626	250	1	0	25072	372323	49242	8300	#DIV/0!	0.000	0.022	-0.67	0.24	-0.87	0.00	0	0.04	10.08	403	#DIV/0!	403
	250	2	5419	28703	404433	53261	10871	2.006	0.013	0.027	0.62	0.64	2.51	2.51	101	0.09	25.42	1017	10.12	1117
	250	3	9007	37834	535562	70511	15526	1.724	0.017	0.029	0.94	0.83	3.53	3.53	141	0.16	40.54	1622	11.48	1763
	250	4	7923	32130	442531	59061	14674	1.852	0.018	0.033	1.03	1.21	4.49	4.49	179	0.24	49.53	1981	11.04	2161
3	250	5	7673	24661	338355	47914	12771	1.664	0.023	0.038	1.47	1.61	6.17	6.17	247	0.36	55.12	2205	8.94	2451
	250	6	6117	21697	286152	39830	10851	1.774	0.021	0.038	1.35	1.63	5.97	5.97	239	0.51	58.48	2339	9.80	2578
	250	7	8154	26487	353357	49918	14908	1.828	0.023	0.042	1.50	2.02	7.02	7.02	281	0.76	62.32	2493	8.87	2774
	250	8	7746	22792	300666	43940	13510	1.744	0.026	0.045	1.74	2.25	7.98	7.98	319	1.26	64.49	2580	8.09	2899
	250	9	8427	27691	345652	50909	15339	1.820	0.024	0.044	1.61	2.21	7.64	7.64	305	2.01	64.54	2582	8.45	2887
	250	10	4888	14455	170692	26780	8179	1.673	0.029	0.048	1.99	2.51	8.99	8.99	360	3.01	66.91	2676	7.44	3036
	250	11	1372	3537	36890	6526	1956	1.426	0.037	0.053	2.74	2.92	11.32	11.32	**453**	5.01	68.07	**2723**	6.01	**3176**
	250	12																	#DIV/0!	0
C848	250	1	3272	19088	273877	35972	6017	1.839	0.012	0.022	0.49	0.18	1.33	1.33	53	0.04	10.85	434	8.16	487
	250	2	5561	25297	389650	51134	10346	1.860	0.014	0.027	0.70	0.61	2.61	2.61	105	0.09	33.74	1349	12.90	1454
	250	3	6033	22556	305362	42126	11233	1.862	0.020	0.037	1.20	1.54	5.47	5.47	219	0.16	55.77	2231	10.19	2450
	250	4	7076	18866	267197	37598	11554	1.633	0.026	0.043	1.81	2.10	7.81	7.81	312	0.24	67.51	2700	8.65	3012
2	250	5	10013	27061	368662	51364	17441	1.742	0.027	0.047	1.86	2.46	8.63	8.63	345	0.36	71.60	2864	8.30	3209
	250	6	4124	11030	139835	21550	7120	1.726	0.029	0.051	2.06	2.77	9.65	9.65	386	0.51	72.91	2916	7.55	3303
	250	7	3071	8361	105145	16578	5497	1.790	0.029	0.052	2.03	2.89	9.84	9.84	394	0.76	74.03	2961	7.52	3355
	250	8	4923	12606	157543	23612	8490	1.725	0.031	0.054	2.21	3.02	10.46	10.46	418	1.26	75.12	3005	7.18	3423
	250	9	3900	10348	125920	19041	6774	1.737	0.031	0.054	2.19	3.01	10.40	10.40	416	2.01	76.26	3050	7.33	3466
	250	10	4121	10264	121921	19240	6668	1.618	0.034	0.055	2.44	3.08	11.03	11.03	441	3.01	77.56	3103	7.03	3544
	250	11	2155	5098	57630	8686	3682	1.709	0.037	0.064	2.73	3.86	13.16	13.16	**527**	5.01	79.47	**3179**	6.04	**3705**
	250	12																	#DIV/0!	0
C578 (500 ppm)	500	1	0	3198	55649	7370	1789	#DIV/0!	0.000	0.032	-0.67	1.17	1.00	1.00	20	0.04	3.31	66	3.31	86
	500	2	3498	9771	154727	21072	5879	1.681	0.023	0.038	1.46	1.64	6.20	6.20	124	0.09	10.65	213	1.72	337
	500	3	2400	2485	24007	4481	2986	1.244	0.100	0.124	7.50	8.21	31.42	31.42	628	0.16	32.87	657	1.05	1286
	500	4	24030	18608	105022	25362	24033	1.000	0.229	0.229	15.03	13.75	57.56	57.56	1151	0.24	61.59	1232	1.07	2383
6	500	5	4112	3403	12192	4178	4114	1.000	0.337	0.337	19.47	18.20	75.35	75.35	1507	0.36	77.41	1548	1.03	3055
	500	6	3132	2083	6754	2827	2738	0.874	0.464	0.405	24.14	19.74	87.77	87.77	1755	0.51	82.87	1657	0.94	3413
	500	7	3317	2247	8297	3040	3213	0.969	0.400	0.387	21.70	19.72	82.85	82.85	1657	0.76	85.15	1703	1.03	3360
	500	8	4812	3615	11324	3910	4743	0.986	0.425	0.419	22.38	20.77	86.30	86.30	1726	1.26	87.08	1742	1.01	3468
	500	9	2581	1757	5174	1933	2132	0.826	0.499	0.412	25.44	19.62	90.11	90.11	1802	2.01	88.95	1779	0.99	3581
	500	10	2479	1746	4885	2318	2414	0.974	0.507	0.494	24.68	22.74	94.85	94.85	1897	3.01	90.58	1812	0.95	3709
	500	11	1350	1029	2543	1422	1542	1.142	0.531	0.606	24.17	26.43	101.19	101.19	**2024**	5.01	95.04	**1901**	0.94	**3925**

Catalyst	**Loading (ppm)**	**Timepoint**	**Well**	**241**	**243**	**245**	**245/241**	**241/243**	**245/243**	**% conv to 241**	**% conv to 245**	**% degen**	**Degen TON**	**Degen TON (no -)**	**% conv**	**Prod TON**
594	5000	1	A11	1	322172	7362	7362	3.1E-06	0.022851	-0.003969536	0.003734621	-0.00047	-0.09396639	-0.09396639	0.04309433	8.61886543
	5000	2	A12	14210	529329	25245	1.776566	0.026845	0.047692	0.021010551	0.02577821	0.093578	18.71550417	18.71550417	0.07350842	14.7016842
	5000	3	A13	39809	587937	48781	1.225376	0.06771	0.08297	0.054870609	0.05349908	0.216739	43.34787565	43.34787565	0.13326473	26.6529463
	5000	4	A14	76844	549046	79051	1.028721	0.139959	0.143979	0.105035133	0.093532512	0.397135	79.42705819	79.42705819	0.26717915	53.4358301
7	5000	5	A15	107075	424545	98808	0.922792	0.252211	0.232739	0.16587236	0.138125667	0.607996	121.5992107	121.5992107	0.45027671	90.0553412
	5000	6	A16	95002	234234	79387	0.835635	0.405586	0.338922	0.22852046	0.175673373	0.808388	161.6775334	161.6775334	0.68510099	137.020199
	5000	7	A17	64587	130516	50267	0.778284	0.494859	0.385141	0.259250317	0.186256095	0.891013	178.2025646	178.2025646	0.80087637	160.175274
	5000	8	A18	37982	69275	29591	0.77908	0.548279	0.427153	0.273576242	0.197626658	0.942406	188.4811601	188.4811601	0.88963711	177.927423
	5000	9	A19	17108	29457	13565	0.792904	0.580779	0.460502	0.280544309	0.206988595	0.975066	195.0131616	195.0131616	0.92193934	184.387868
Catalyst	Loading (ppm)	Timepoint	Well	241	243	245	245/241	241/243	245/243	% conv to 241	% conv to 245	% degen	Degen TON	Degen TON (no -)	% conv	Prod TON
	1000	1	A11	6702	578003	13854	2.067144	0.011595	0.023969	0.00722432	0.004539638	0.023528	23.52791566	23.52791566	0.01440203	14.4020288
	1000	2	A12	44401	778283	58336	1.313844	0.05705	0.074955	0.046424696	0.047608211	0.188066	188.0658126	188.0658126	0.04408062	44.0806242
	1000	3	A13	87649	896866	103094	1.176214	0.097728	0.114949	0.076616133	0.076183629	0.3056	305.5995251	305.5995251	0.06326821	63.2682051
8	1000	4	A14	183666	928632	188083	1.024049	0.197781	0.202538	0.137267573	0.126030891	0.526597	526.5969278	526.5969278	0.11485188	114.851878
	1000	5	A15	256406	857032	242160	0.94444	0.299179	0.282557	0.185173474	0.160031079	0.690409	690.4091059	690.4091059	0.19232079	192.320791
	1000	6	A16	323434	904493	294691	0.911132	0.357586	0.325808	0.20844709	0.174936356	0.766767	766.7668936	766.7668936	0.23860197	238.601967
	1000	7	A17	342749	812027	303839	0.886477	0.422091	0.374174	0.231009929	0.18970056	0.841421	841.4209782	841.4209782	0.27592383	275.923827
	1000	8	A18	367784	801372	316595	0.860818	0.458943	0.395066	0.243568235	0.194481572	0.8761	876.0996147	876.0996147	0.33640958	336.40958
	1000	9	A19	276878	509168	218307	0.788459	0.543785	0.428752	0.271705403	0.198754878	0.940921	940.9205615	940.9205615	0.54449029	544.490292

Figure S7 (cont.). Data for RCM of **9-d_2**.

Catalyst	Cat Loading (ppn	Timepoir	m / z = 227	m / z = 229	m / z = 233	m / z = 235	229 / 227	233 / 235	233 / 229	% conv to 22	% conv to 23	% degen	% degen w / o negatives	Degen TON	t(h)	% conv	Productive TON
Stock Solution		0	230007	4396	1513	184986	0.019	0.008	0.344	1.88	0.81	5.37					
C626	500	1	616791	7764	3068	436149	0.013	0.007	0.395	-0.63	-0.11	-1.49	0.00	0	0.04	2.46	49
	500	2	391014	5751	2572	273238	0.015	0.009	0.447	-0.43	0.12	-0.61	0.00	0	0.09	6.35	127
	500	3	656837	10270	4416	476236	0.016	0.009	0.430	-0.34	0.11	-0.46	0.00	0	0.16	11.78	236
	500	4	435998	6192	5445	306387	0.014	0.018	0.879	-0.48	0.93	0.92	0.92	18	0.24	17.64	353
	500	5	647357	10285	8969	455957	0.016	0.020	0.872	-0.31	1.12	1.61	1.61	32	0.36	23.91	478
3	500	6	402334	6667	7246	280810	0.017	0.026	1.087	-0.25	1.70	2.92	2.92	58	0.51	29.43	589
	500	7	616022	10278	12273	433455	0.017	0.028	1.194	-0.23	1.94	3.42	3.42	68	0.76	34.94	699
	500	8	410521	8138	11713	288190	0.020	0.041	1.439	0.07	3.09	6.33	6.33	127	1.26	40.61	812
	500	9	525931	9506	14600	354566	0.018	0.041	1.536	-0.10	3.14	6.09	6.09	122	2.01	45.66	913
	500	10	244954	5151	8411	160820	0.021	0.052	1.633	0.18	4.16	8.69	8.69	174	3.01	50.81	1016
	500	11	524060	11036	19305	344018	0.021	0.056	1.749	0.19	4.50	9.38	9.38	188	5.01	58.80	1176
	500	12	60520	1545	3617	40251	0.026	0.090	2.341	0.61	7.43	16.10	16.10	322	8.01	68.80	**1376**
C848	500	1															
	500	2	385098	5477	2783	275995	0.014	0.010	0.508	-0.47	0.19	-0.57	0.00	0	0.09	10.10	202
	500	3	512096	7652	5313	353163	0.015	0.015	0.694	-0.40	0.67	0.54	0.54	11	0.16	16.44	329
	500	4	520906	8275	6999	365961	0.016	0.019	0.846	-0.31	1.07	1.51	1.51	30	0.24	21.54	431
2	500	5	343007	5476	5707	240241	0.016	0.024	1.042	-0.30	1.51	2.41	2.41	48	0.36	25.40	508
	500	6	394037	6579	6740	275163	0.017	0.024	1.024	-0.23	1.58	2.69	2.69	54	0.51	27.49	550
	500	7	511458	9034	8831	354580	0.018	0.025	0.978	-0.14	1.62	2.96	2.96	59	0.76	29.17	583
	500	8	491550	7895	8727	344183	0.016	0.025	1.105	-0.29	1.66	2.73	2.73	55	1.26	30.86	617
	500	9	394299	7079	7617	273369	0.018	0.028	1.076	-0.11	1.90	3.58	3.58	72	2.01	33.15	663
	500	10	496771	8362	9844	339709	0.017	0.029	1.177	-0.22	2.00	3.57	3.57	71	3.01	35.77	715
	500	11	473355	7820	10500	321590	0.017	0.033	1.343	-0.25	2.35	4.20	4.20	84	5.01	40.43	809
	500	12	109444	2062	3630	74803	0.019	0.049	1.760	-0.03	3.82	7.58	7.58	152	8.01	46.64	933
C712 (0.1 M)	500	1	483752	6681	2184	339084	0.014	0.006	0.327	-0.51	-0.17	-1.37	0.00	0	0.04	0.00	0
	500	2	862925	11974	4151	620138	0.014	0.007	0.347	-0.51	-0.15	-1.31	0.00	0	0.09	0.00	0
	500	3	505817	6755	3274	358614	0.013	0.009	0.485	-0.56	0.09	-0.93	0.00	0	0.16	1.39	28
	500	4	322994	4199	1702	225888	0.013	0.008	0.405	-0.59	-0.06	-1.31	0.00	0	0.24	2.25	45
	500	5	244249	3653	2350	168745	0.015	0.014	0.643	-0.40	0.56	0.32	0.32	6	0.36	3.64	73
5	500	6	566303	9552	6193	394152	0.017	0.016	0.648	-0.22	0.74	1.04	1.04	21	0.51	5.67	113
	500	7	610879	9232	9697	419933	0.015	0.023	1.050	-0.39	1.45	2.12	2.12	42	0.76	9.21	184
	500	8	333864	5037	8483	226428	0.015	0.037	1.684	-0.39	2.80	4.82	4.82	96	1.26	15.14	303
	500	9	337309	6399	12282	227463	0.019	0.054	1.919	-0.01	4.31	8.60	8.60	172	2.01	22.24	445
	500	10	681974	13480	31363	449898	0.020	0.070	2.327	0.06	5.71	11.54	11.54	231	3.01	28.92	578
	500	11	435973	9426	27307	275000	0.022	0.099	2.897	0.24	8.22	16.93	16.93	339	5.01	37.04	741
	500																
C712 (0.05 M)	500	1	686896	9167	1699	489930	0.013	0.003	0.185	-0.56	-0.47	-2.05	0.00	0	0.04	0.00	0
	500	2	387457	4741	1780	270762	0.012	0.007	0.375	-0.67	-0.16	-1.65	0.00	0	0.09	0.00	0
	500	3	359300	4724	1440	256132	0.013	0.006	0.305	-0.58	-0.25	-1.66	0.00	0	0.16	0.00	0
	500	4	376098	6289	1757	268981	0.017	0.007	0.279	-0.23	-0.16	-0.79	0.00	0	0.24	0.00	0
	500	5	480011	6757	1802	337913	0.014	0.005	0.267	-0.49	-0.28	-1.54	0.00	0	0.36	0.00	0
5	500	6	523001	7098	3458	368030	0.014	0.009	0.487	-0.54	0.12	-0.83	0.00	0	0.51	0.00	0
	500	7	408578	5886	3511	293417	0.014	0.012	0.597	-0.46	0.37	-0.17	0.00	0	0.76	4.58	92
	500	8	258269	3737	3499	178306	0.014	0.020	0.936	-0.45	1.11	1.33	1.33	27	1.26	8.18	164
	500	9	342276	6055	7427	233799	0.018	0.032	1.227	-0.14	2.27	4.26	4.26	85	2.01	13.47	269
	500	10	463710	8062	13518	311013	0.017	0.043	1.677	-0.17	3.35	6.38	6.38	128	3.01	19.17	383
	500	11	437464	9327	18992	280143	0.021	0.068	2.036	0.21	5.54	11.50	11.50	230	5.01	27.14	543
	500	12	468790	9987	25492	303805	0.021	0.084	2.553	0.21	6.93	14.28	14.28	286	8.01	34.34	687
C571	500	1	406017	5908	1212	288751	0.015	0.004	0.205	-0.44	-0.39	-1.67	0.00	0	0.04	0.00	0
	500	2	628888	8739	3041	445863	0.014	0.007	0.348	-0.50	-0.13	-1.28	0.00	0	0.09	2.37	47
	500	3	381776	5306	1527	274173	0.014	0.006	0.288	-0.50	-0.26	-1.52	0.00	0	0.16	4.65	93
	500	4	612272	7888	1956	431224	0.013	0.005	0.248	-0.60	-0.36	-1.93	0.00	0	0.24	7.40	148
	500	5	562011	8012	2461	399344	0.014	0.006	0.307	-0.47	-0.20	-1.34	0.00	0	0.36	10.58	212
4	500	6															
	500	7	371497	5549	1942	267065	0.015	0.007	0.350	-0.40	-0.09	-0.99	0.00	0	0.76	17.63	353
	500	8	388312	6264	2397	278144	0.016	0.009	0.383	-0.29	0.04	-0.49	0.00	0	1.26	21.42	428
	500	9	252841	4220	1691	178113	0.017	0.009	0.401	-0.23	0.13	-0.21	0.00	0	2.01	23.89	478
	500	10	506601	8204	3589	358869	0.016	0.010	0.437	-0.28	0.18	-0.21	0.00	0	3.01	25.01	500
	500	11	474695	7519	3614	341770	0.016	0.011	0.481	-0.32	0.24	-0.16	0.00	0	5.01	25.48	510
	500	12	195090	3049	1118	136757	0.016	0.008	0.367	-0.34	0.00	-0.67	0.00	0	8.01	25.61	512
C823	2000	1	230591	5573	3759	163067	0.024	0.023	0.675	0.48	1.44	3.85	3.85	19	0.04	5.73	29
	2000	2	465022	8213	8410	318139	0.018	0.026	1.024	-0.14	1.76	3.25	3.25	16	0.09	8.14	41
	2000	3	937088	21291	18907	648863	0.023	0.029	0.888	0.35	2.02	4.73	4.73	24	0.15	10.93	55
	2000	4	425592	10972	12269	283654	0.026	0.043	1.118	0.64	3.33	7.95	7.95	40	0.24	13.95	70
	2000	5	564761	16122	18823	378802	0.029	0.050	1.168	0.90	3.92	9.65	9.65	48	0.35	17.37	87
1	2000	6	393130	12027	14556	261486	0.031	0.056	1.210	1.09	4.46	11.11	11.11	56	0.50	20.89	104
	2000	7	366392	12573	17476	236355	0.034	0.074	1.390	1.44	6.07	15.03	15.03	75	0.75	25.43	127
	2000	8	358872	12598	20303	224306	0.035	0.091	1.612	1.52	7.49	18.01	18.01	90	1.25	31.69	158
	2000	9	329167	11939	20642	198544	0.036	0.104	1.729	1.62	8.61	20.46	20.46	102	2.00	37.88	189
	2000	10	146611	6428	10920	87357	0.044	0.125	1.699	2.32	10.30	25.25	25.25	126	3.00	43.60	218
	2000	11	291776	12166	24120	162763	0.042	0.148	1.983	2.13	12.10	28.45	28.45	142	5.00	50.56	253
	2000	12	123266	5595	11924	67893	0.045	0.176	2.131	2.47	14.13	33.19	33.19	166	8.00	55.97	280
C578 (1000ppm)	1000	1	450660	6484	3292	315589	0.014	0.010	0.508	-0.46	0.22	-0.47	0.00	0	0.04	0.00	0
	1000	2	397911	6684	4801	276910	0.017	0.017	0.718	-0.22	0.89	1.34	1.34	13	0.09	0.00	0
	1000	3	233054	4534	4664	156205	0.019	0.030	1.029	0.03	2.09	4.24	4.24	42	0.16	2.98	30
	1000	4	381852	8558	11839	251272	0.022	0.047	1.383	0.32	3.69	8.01	8.01	80	0.24	5.44	54
	1000	5	252203	8819	15764	158737	0.035	0.099	1.788	1.50	8.22	19.45	19.45	195	0.36	11.54	115
6	1000	6	221621	11813	24957	128715	0.053	0.194	2.113	3.19	15.43	37.23	37.23	372	0.51	20.79	208
	1000	7	325745	24475	54672	171706	0.075	0.318	2.234	5.11	23.34	56.91	56.91	569	0.76	31.46	315
	1000	8	43460	4507	11004	22225	0.104	0.495	2.442	7.52	32.30	79.65	79.65	797	1.26	41.98	420
	1000	9	71555	7516	21111	29187	0.105	0.723	2.809	7.63	41.16	97.58	97.58	976	2.01	51.05	511
	1000	10	51693	6330	17893	18534	0.122	0.965	2.827	9.03	48.31	114.69	114.69	1147	3.01	58.97	590
	1000	11	7665	885	3207	2467	0.115	1.300	3.624	8.48	55.71	128.37	128.37	1284	5.01	69.01	690

Catalysts	Loading	time (min)	Timepoint	227	229	233	235	229/227	233/235	233/229	conv. to 229	conv. to 233	degen	Degen TON	conv.	Conv. TON
	2500		B1	863895	27881	11356	874845	0.032274	0.012981	0.407302	-0.026699396	-0.005120157	-0.06364	-25.45564195	0.00576	2.30399028
	2500		B2	893168	32435	21367	903552	0.036315	0.023648	0.658764	-0.022921952	0.005167077	-0.03551	-14.2039001	0.014547	5.81885662
	2500		B3	884959	43518	39722	894835	0.049175	0.04439	0.912772	-0.011093669	0.024569155	0.026951	10.78038924	0.012692	5.07692212
	2500		B4	873783	60976	68603	883935	0.069784	0.077611	1.125082	0.007267813	0.054086868	0.122709	49.08374555	0.017846	7.13846034
	2500		B5	888667	78565	99441	895590	0.088408	0.111034	1.265716	0.023262661	0.082003185	0.210532	84.21267637	0.025343	10.1370328
8	2500		B6	893121	123347	169573	894483	0.138108	0.189577	1.374764	0.063384657	0.141430327	0.40963	163.8519877	0.03782	15.1279406
	2500		B7	779679	124670	187328	775836	0.159899	0.241453	1.502591	0.079892098	0.176557914	0.5129	205.1600091	0.05438	21.7519262
	2500		B8	826162	202179	316340	808757	0.244721	0.391143	1.564653	0.138642989	0.263232463	0.803751	321.5003613	0.08671	34.6839083
	2500		B9	802979	245027	387233	778891	0.305147	0.497159	1.580369	0.175839077	0.314134054	0.979946	391.978505	0.111103	44.4410198
	2500		B10	840661	297103	462698	807732	0.353416	0.572836	1.557366	0.203164872	0.346271415	1.098873	439.5490296	0.130363	52.1453155
	2500		B11	794077	355596	554315	741943	0.44781	0.747113	1.558834	0.251337889	0.409692657	1.322061	528.8244364	0.183387	73.3549932
	2500		B12	746771	370991	582221	665514	0.496794	0.874844	1.569367	0.273941208	0.448687914	1.445258	578.1032983	0.235989	94.3957155
	5000	17	A1	716987	21882	10862	732889	0.030519	0.014821	0.49639	-0.02834844	-0.003330055	-0.06336	-12.67139786	0.021104	4.220828
	5000	39	A2	673242	29905	27153	681568	0.044419	0.039839	0.907975	-0.015433749	0.020378274	0.009889	1.977809925	0.021565	4.31290139
	5000	90	A3	712983	54868	88665	713854	0.076956	0.124206	1.615969	0.013492598	0.09254896	0.212083	42.41662335	0.055557	11.1114632
7	5000	138	A4	586921	206484	429294	487257	0.351809	0.881042	2.079067	0.202286466	0.450445423	1.305464	261.0927556	0.409495	81.8990412
	5000	242	A5	466090	161814	412637	234785	0.347173	1.75751	2.55007	0.199741026	0.619419593	1.638321	327.6642474	0.686526	137.30519
	5000	372	A6	277851	76995	251605	90725	0.277109	2.773271	3.26781	0.159017478	0.71704354	1.752122	350.424407	0.83573	167.146088
	5000	483	A7	95622	23636	85857	26239	0.247182	3.272114	3.632467	0.140228181	0.747989446	1.776435	355.2870508	0.942149	188.429755
	5000	724	A8	15298	3780	12958	4995	0.247091	2.594194	3.428042	0.140170003	0.703839114	1.688018	337.6036469	0.983691	196.738104

Figure S8. Data for RCM of **13-*d*$_0$** + **13-*d*$_8$**.

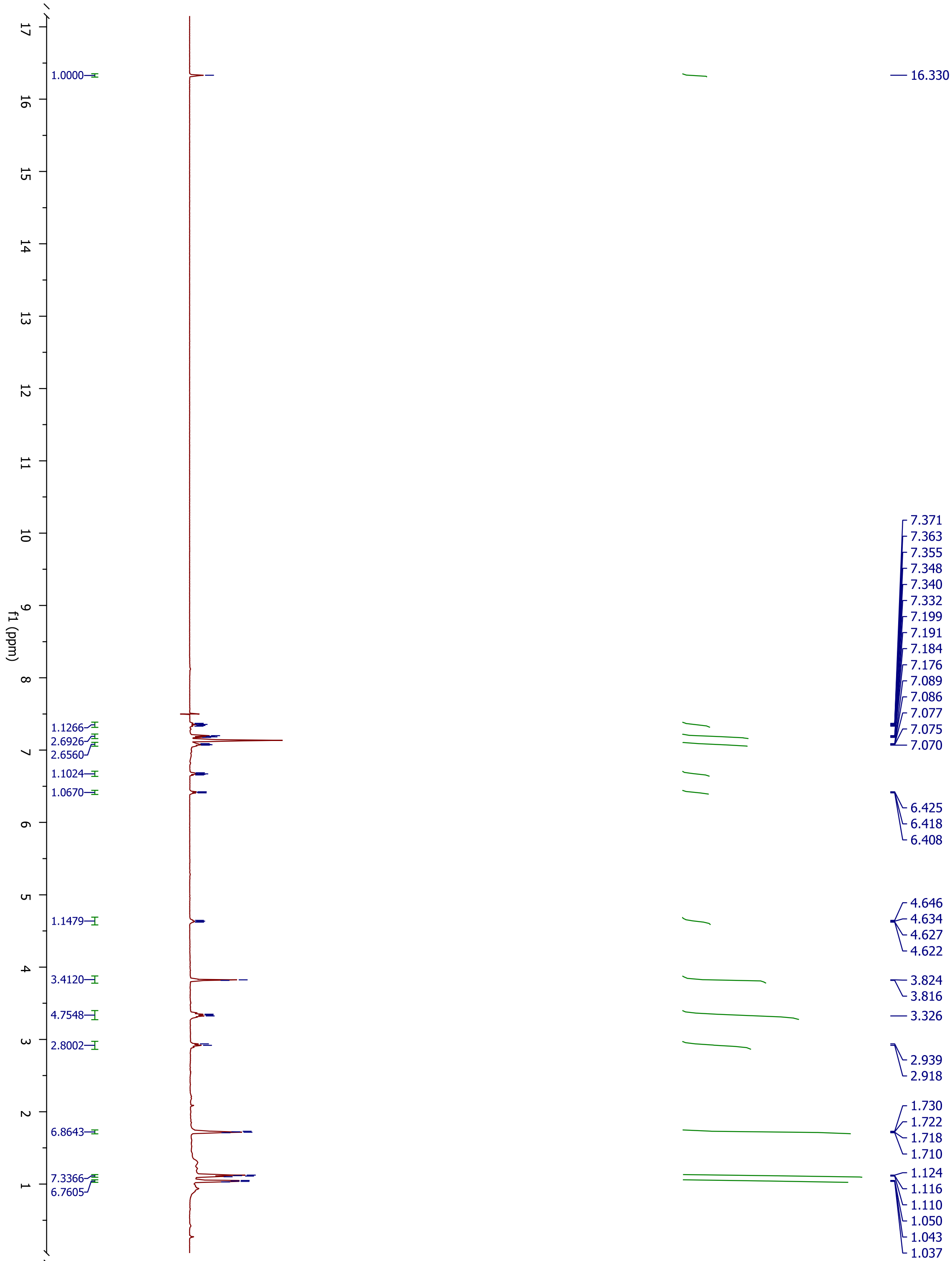


Figure S9. ^{1}H NMR spectrum of **7** (C_6D_6, 600 MHz).

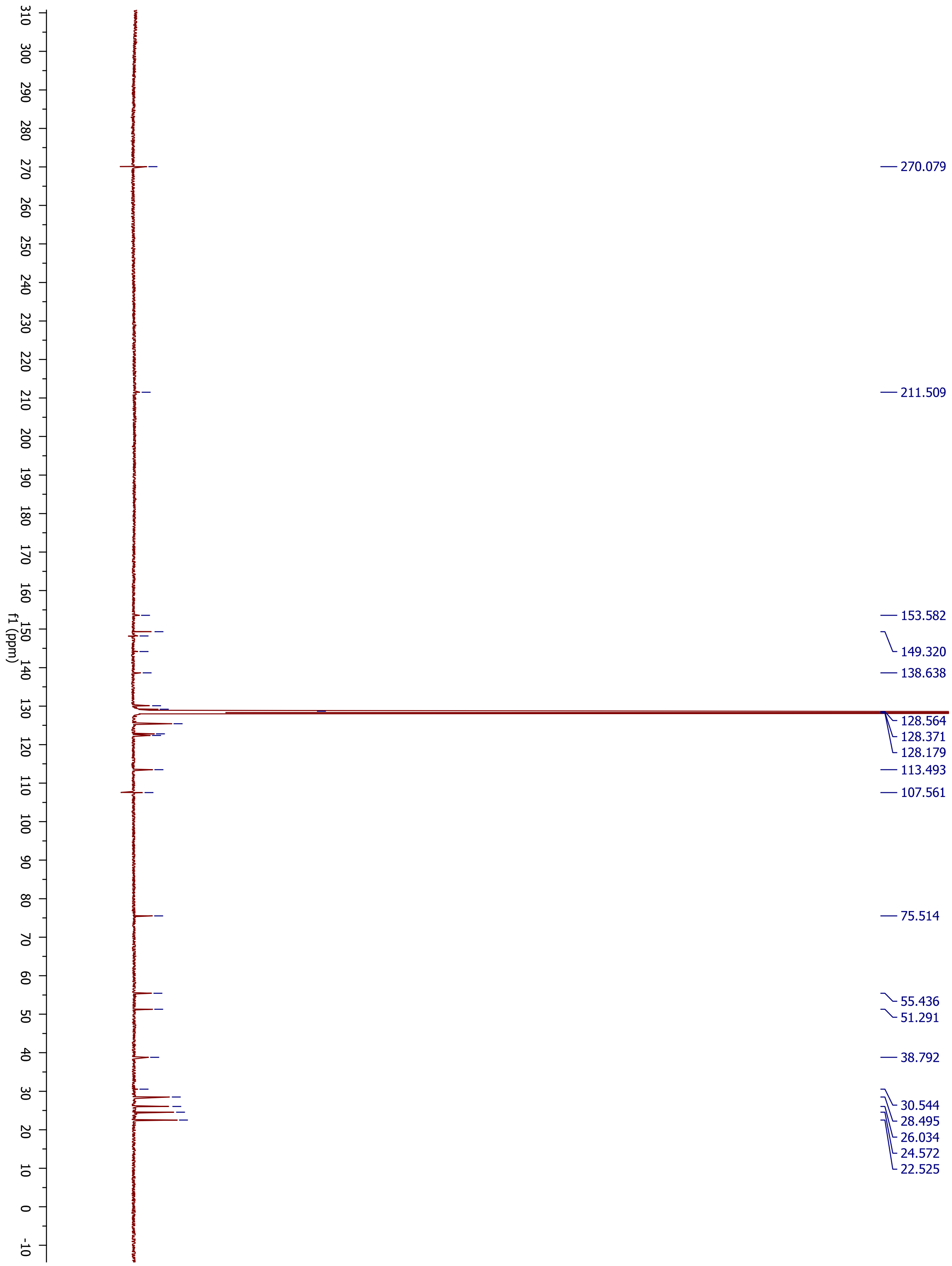


Figure S10. ^{13}C NMR spectrum of **7** (C_6D_6, 600 MHz).

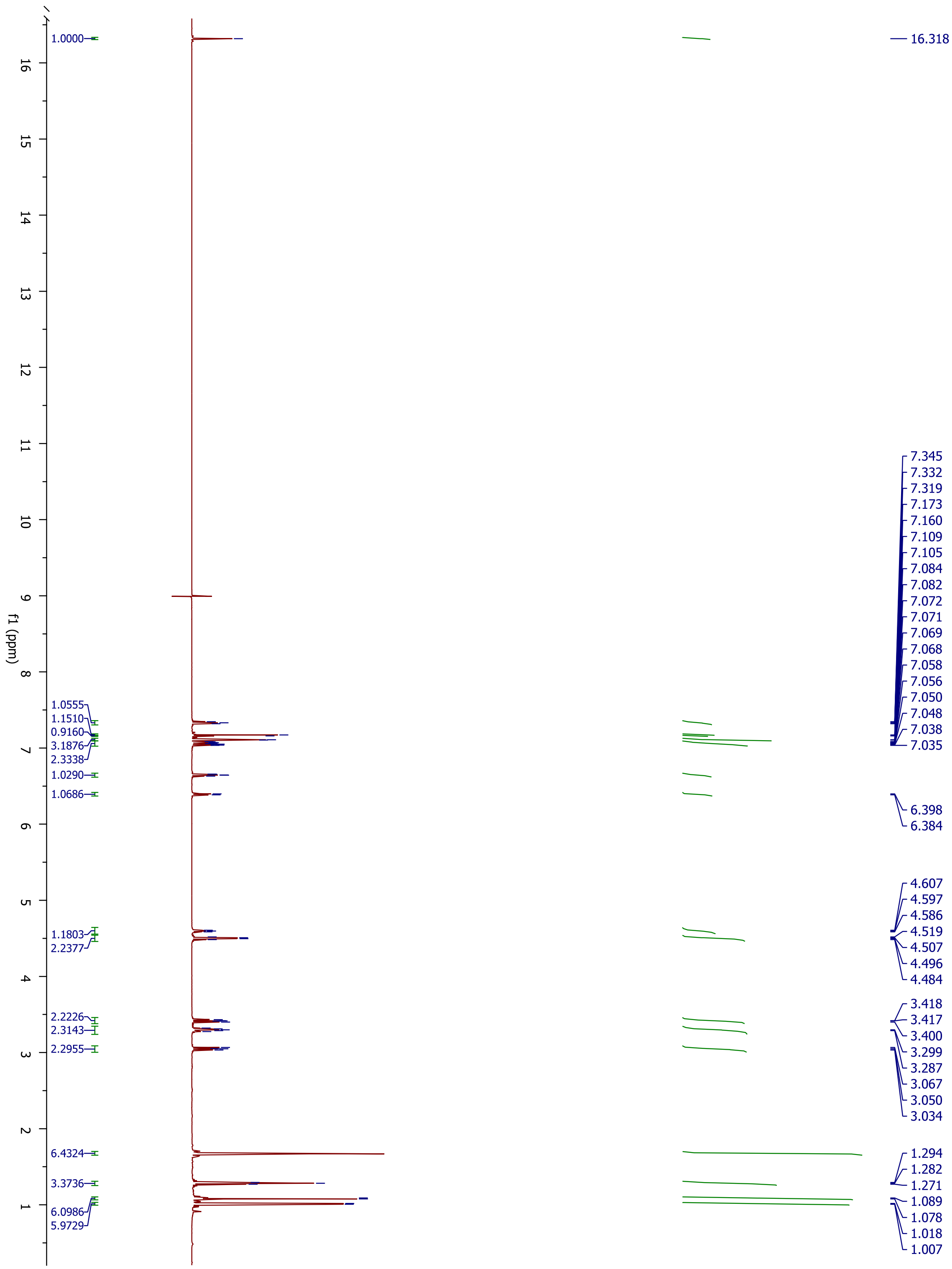


Figure S11. ^{1}H NMR spectrum of **8** (C_6D_6, 600 MHz).

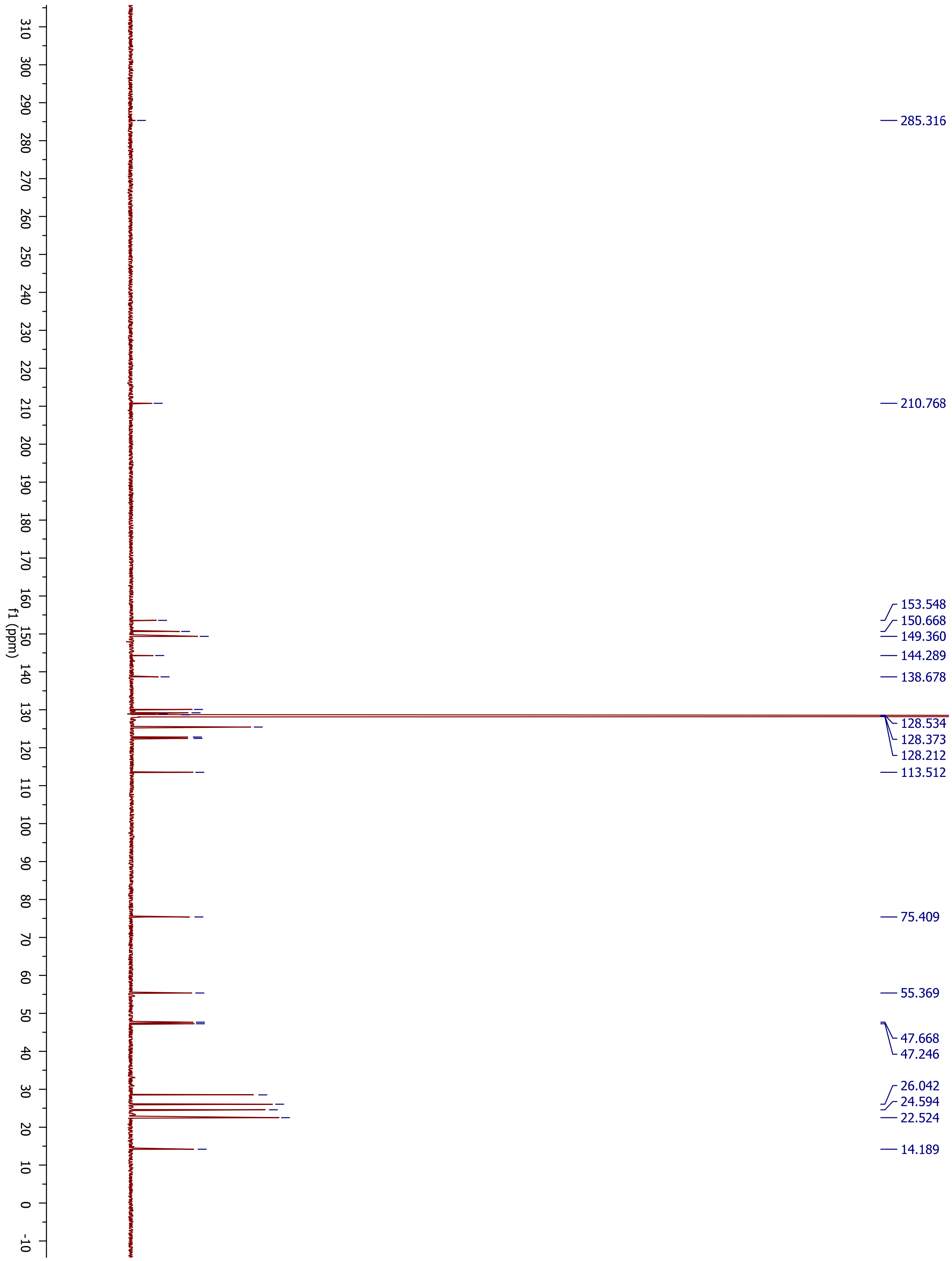


Figure S12. ^{13}C NMR spectrum of **8** (C_6D_6, 600 MHz).

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(1) Love, J.A.; Morgan, J.P.; Trnka, T.M.; Grubbs, R.H., *Angew. Chem. Int. Ed.* **2002**, *41*, 4035.
(2) Blum, A. P.; Ritter, T.; Grubbs, R. H. *Organometallics* **2007**, *26*, 2122.

(3) Anderson, D. R.; Lavallo, V.; O'Leary, D. J.; Bertrand, G.; Grubbs, R. H. *Angew. Chem.-Int. Edit.* **2007**, *46*, 7262.
(4) Marshall, C.; Ward, M. F.; Skakle, J. M. S. *Synthesis* **2006**, 1040.
(5) Kolsaker, P.; Kvarsnes, A.; Storesund, H. *Org. Mass. Spec.* **1986**, *21*, 535.
(6) van der Eide, E. F.; Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2008**, *130*, 4485.
(7) Kisanga, P.; Widenhoefer, R.A. *J. Am. Chem. Soc.* **2000**, *122*, 10017.